Process chlorination

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PROVISIONAL SPECIFICATION.

Improvements in the Treatment of Sulphide Ores.

We, JAMES SWINBURNE, of 82, Victoria Street, London, S.W., Engineer, and EDGAR ARTHUR ASHCROFT of same address, Metallurgist, do hereby declare the nature of this invention to be as follows:—

Our invention has reference to the treatment of sulphide ores or products with chlorine, for the purpose of separating the valuable from the worthless constituents, and the resulting metallic chlorides may be electrolysed so as to constitute a cyclic process.

The process is applicable to various sulphides but we will describe it specially in connection with mixed lead-zinc sulphide ores.

The ore is ground finely, and it is made into a cream with fused chloride of zinc, or preferably a mixture of chloride of zinc with sodium or potassium chloride. The cream is put into a converter of special design in which it is treated with chlorine, the gas being forced in at the bottom (in a manner similar to the converter used for treatment of copper and other ores or mattes by air blast). At a suitable temperature the chlorine is rapidly absorbed by the metals and sulphur is given off in its place. The re-action is most vigorous at a high temperature and being exothermic the temperature may be regulated by increasing or decreasing the blast of chlorine. If desired, the operation may be pushed so far as to more or less completely volatilize the zinc and the other metallic chlorides leaving the gangue behind as a residue, associated only with small quantities of chlorides. To start the operation it is most convenient to fuse the chlorides *etc.*, in a separate vessel or furnace. The treatment is carried on till all or nearly all the sulphides are converted into chlorides, and the iron which is practically always present, may also be all converted into the ferric state and in this state it is readily precipitated as Fe_2O_3 by the addition of ZnO (roasted zinc ore) to the pot. During nearly the whole of the process the chlorine is completely absorbed, sulphur, (and at certain temperatures sulphur chloride) being liberated. These are collected and condensed. Towards the end a little excess of chlorine may be necessary to make sure of oxidizing all the iron to the ferric state. Any chlorine that passes over at this stage may be returned to the chlorine store after condensation of the sulphur. The sulphur is comparatively pure and may be sold for any common purpose. If it is associated with important quantities of metallic chlorides, as will be the case when conducting the process at high temperatures the chlorides may be dissolved in water, leaving the insoluble sulphur behind. At the end of the treatment the converter contains varying quantities of fused chlorides of zinc lead, silver and iron and all the gangue. If zinc oxide has been added to the charge the iron is all present as ferric oxide and the gangue and the iron may now be allowed to settle, preferably in a separate vessel or furnace, and the clear chlorides poured off. The fused chlorides may then be treated with metallic lead or zinc which removes all the metals which will part with their

[*Price 8d.*]

chlorine to lead, such as silver and gold and antimony. The lead which is now rich in silver, and in some cases gold, may be then run off to be treated for the precious metals. The fused chlorides may then be treated with zinc, which takes out the lead by substitution. The fused mass then contains zinc, and potassium chlorides and some trace of chlorides of manganese and other metals (or the mixed chlorides may be electrolysed without previous treatment with lead and zinc in which case the silver-lead and zinc will separate progressively and may be drawn off from the electrolysis bath at suitable intervals in a more or less divided state. Instead of precipitating the iron when the charge is in the converter, the fused chlorides may be dissolved in water and the solution treated for the removal of iron, by means of zinc oxide or otherwise, the iron being brought to the ferric state by chlorine. The resulting solution of zinc and sodium or potassium chloride is then evaporated down and fused, and electrolysed to extract the zinc with or without the previous precipitation of silver by lead and lead by zinc, as above described. The double chlorides of sodium or potassium and zinc are preferred because they decompose little on drying and are very fusible. They also fume but little on melting and exposure to the air.

As to the mixture of gangue and fused chlorides from which the clear chlorides have been described as having been poured off or partially distilled off, the cream may be treated with lead and then with zinc in the same way as the clear chlorides. On dissolving in water there will be found some small globules of lead or zinc which have been mixed with the gangue; but they are easily separated under water. Or the chlorides may be distilled from the gangue by heating. The more or less pure product of ZnK_2Cl_4 resulting from the above operations is conveniently treated by electrolysis in the fused state, the resulting zinc may be collected as molten metal and the chlorine drawn off to be used for the converters. The electrolysis is best carried on in a vat which is heated and kept hot by the electric current, which causes the decomposition of the chloride: the volts necessary at the terminals of the bath will depend to a large extent on the means employed to conserve the heat in the bath. With large vats from 2·5 to 5 volts will be required.

The chlorine from the electrolysis vat may be pumped direct to the converter, but preferably it is cooled and compressed and stored in the liquid state. The storage may be assisted by cooling to a low temperature such as—30° C.

This converter method of treating sulphides with chlorine is applicable to other sulphides, such as iron, copper, nickel, cobalt, antimony *etc.* In the case of iron pyrites ores particularly, these ores can be treated in conjunction with oxidised zinc ores. The sulphur is first expelled and the iron chloride raised to the ferric state by chlorine. The iron is then precipitated as Fe_2O_3 by the addition of oxidised zinc ore. The resulting zinc chloride is then removed and electrolysed as before. The residue of ferric oxide may also constitute a valuable product as iron ore or paint.

An operation analogous to the above may be carried on by placing the cream in a revolving furnace of form similar to a Bruckner roasting cylinder, contracted at the ends. The gas is admitted through a pipe leading into the centre door and the sulphur distils off through a similar pipe in the other end door. The doors can be removed and a movable fire box and flue substituted to heat the charge initially.

Dated this 11th day of July 1899.

JAMES SWINBURNE,
EDGAR A. ASHCROFT.

COMPLETE SPECIFICATION.

Improvements in the Treatment of Sulphide Ores.

We, JAMES SWINBURNE, Engineer, and EDGAR ARTHUR ASHCROFT, Mining Engineer, both of Grosvenor Mansions, 82, Victoria Street, Westminster, in the County of London, do hereby declare the nature of this invention and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

Our invention has reference to the treatment of sulphide ores or products with chlorine, for the purpose of separating the valuable from the worthless constituents, and the resulting metallic chlorides may be electrolysed so as to constitute a cyclic process.

The process is applicable to the numerous sulphide ores in which the various metals are contained single or together, but we will describe it particularly in connection with mixed lead-zinc silver sulphide ores, such as the well known Broken Hill ores.

In carrying this invention into effect, the ore is crushed and it is made into a cream with fused chloride of zinc, or a mixture of chloride of zinc with sodium or potassium chloride. The cream is put into a converter or suitable vessel in which it is treated with chlorine, the gas being forced in at the bottom. At a suitable temperature for instance a low red heat, the chlorine is rapidly absorbed by the metals and sulphur is given off in its place. The reaction is most vigorous at high temperatures well above the fusing point of zinc chloride, and being exothermic, the temperature may be maintained and regulated by increasing or decreasing the blast of chlorine. If desired the operation may be pushed so far as to more or less completely volatilize the zinc and the other metallic chlorides, leaving the gangue behind as a residue, associated only with small quantities of chlorides. To start furnace, the converter being heated by internal action. The treatment is carried the operation it is convenient to fuse the chlorides *etc.* in a separate vessel or on till all or nearly all the sulphides are converted into chlorides. Fresh supplies of sulphides are added to the converter and the operation is carried on until the residual gangue has accumulated so as to make the mixture with the remaining chloride too thick for working. The iron which is practically always present, may also be all converted into the ferric state by chlorine, and in this state it is really precipitated as Fe_2O_3 by the addition of ZnO (roasted zinc ore) to the pot. Manganese is also precipitated as oxide by passing in chlorine in the presence of zinc oxide. Or manganese and iron are both precipitated by blowing in air in the presence of zinc oxide. This zinc oxide may be made from the sulphide if desired by oxidising a portion of the sulphur of the ore by means of the air blast instead of carrying the decomposition of the sulphide to completion by means of the chlorine blast. During nearly the whole of the process the chlorine is completely absorbed, sulphur being liberated. This is collected and condensed. Towards the end a little excess of chlorine may be necessary to make sure of oxidising all the iron to the ferric state. Any chlorine that passes over at this stage may be returned to the chlorine store after condensation of the sulphur, taking care to avoid the formation of chloride of sulphur by keeping the chlorine from coming into contact with the sulphur. The sulphur is comparatively pure and may be sold for any common purpose. If it is associated with important quantities of metallic chlorides, as will be the case when conducting the process at high temperatures, the chlorides may be dissolved in water, leaving the insoluble sulphur behind, or they may be separated by fractional distillation. At the end of the treatment the converter contains varying quantities of fused

chlorides of zinc lead, silver, iron and manganese and all the gangue. If zinc oxide has been added to the charge the iron and manganese are present as oxides, the gangue and the iron and manganese oxides may be allowed to settle, preferably in a separate vessel or furnace, and the other chlorides poured off. The fused chlorides may then be treated with metallic lead, which removes all the metals which will part with their chlorine to lead, such as silver and gold and antimony. The excess lead, which is now rich in silver, and in some cases gold, may be then run off to be treated for the precious metals. The fused chlorides may then be treated with zinc, which takes out the lead by substitution. The fused mass then contains zinc chloride or zinc and sodium or potassium chlorides and some traces of chlorides of iron and manganese and other metals. Or the mixed chlorides may be fractionally electrolysed without precious treatment with lead or zinc, in which case the silver-lead and the zinc will separate progressively and may be drawn off from the electrolysis bath at suitable intervals. Instead of precipitating the iron and manganese when the charge is fused, the chlorides after the extraction of lead and precious metals, may be dissolved in water and the solution treated for the removal of iron and manganese by means of zinc oxide or otherwise, the iron being brought to the ferric state by chlorine. The resulting solution of zinc chloride or zinc and sodium or potassium chlorides is then evaporated down and fused and electrolysed to extract the zinc. The double chlorides of sodium or potassium and zinc are preferred for electrolysis because they decompose little on drying and are more fusible and conduct better. They also fume but little on melting and exposure to the air. But simple chloride of zinc is preferred in the converter. As to the mixture of gangue and fused chlorides from which the clear chlorides have been poured off or partially distilled off, the cream may be treated with lead and then with zinc in the same way as the clear chlorides. The zinc chloride or the zinc and potassium or sodium chlorides may be dissolved out in water, when some small globules of lead or zinc which have been mixed with the gangue, and which are easily separated under water may be observed. Or the chlorides may be distilled from the gangue by heating. The more or less pure product of zinc chloride resulting from the above operations is conveniently treated by electrolysis in the fused state, the resulting zinc may be collected as molten metal and the chlorine drawn off to be used for the converters. The electrolysis is best carried on in a vat which is heated and kept hot by the electric current which causes the decomposition of the chloride; the pressure necessary at the terminals of the bath will depend to a large extent on the means employed to conserve the heat in the bath.

The chlorine from the electrolysis vat may be pumped direct to the converter, but preferably it is cooled and compressed, and stored in the liquid state. The storage may be assisted by cooling to a low temperature. This converter method of treating sulphides with chlorine is applicable to the treatment of other sulphides, such as iron, copper, nickel, cobalt, antimony *etc.*

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Treating sulphide ores, suspended in or mixed with a fused chloride or chlorides with chlorine, substantially as described.
2. Treating metallic sulphides with a fused chloride or chlorides and passing chlorine through the mixture, substantially as described.
3. Obtaining sulphur from sulphide ores by passing chlorine through a mixture of the ore and a fused salt, substantially as described.
4. Treating ore mixed with chloride in a converter heated essentially by the chemical action of the chlorine.
5. The cyclic process of treating ores suspended in fused salt with chlorine and electrolytically decomposing the resulting chlorides into metal and chlorine.

Swinburne and Ashcroft's Improvements in the Treatment of Sulphids Ores.

6. As a step in the herein described process, separating from the fused chlorine treated charge, iron and manganese, by precipitation as oxide substantially as described.

Dated this 23rd day of March 1900.

EDGAR A. ASHCROFT.
Boult, Wade & Kilburn,
Agents for the Applicants.

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